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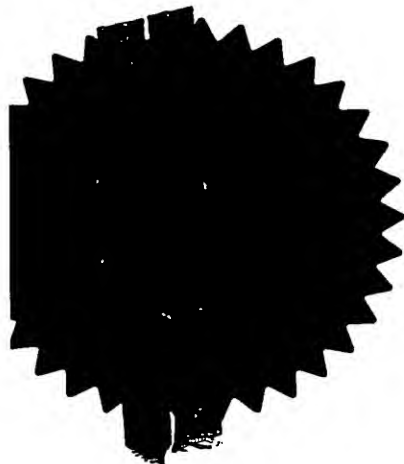


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DC5165

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DOW CORNING CORPROATION  
Midland  
Michigan 48611  
USA

850 604 0002

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

USA/Michigan

## 4. Title of the invention

METHOD OF MAKING KAOLIN CONTAINING SILICONE RUBBER COMPOSITIONS

## 5. Name of your agent (if you have one)

A M Donlan

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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Intellectual Property Department  
Cardiff Road  
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Patents ADP number (if you know it) 41403 7001

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## METHOD OF MAKING KAOLIN CONTAINING SILICONE RUBBER COMPOSITIONS

[0001] This invention is related to a method of producing highly filled silicone rubber compositions containing a treated kaolin. In particular, it relates to the use of kaolin as substantially the only filler in the silicone rubber composition.

[0002] Silicone rubber, often referred to as silicone elastomer, is composed of three essential ingredients. These ingredients are (i) a substantially linear high molecular weight silicone polymer, (ii) one or more filler(s), and (iii) a crosslinking agent, sometimes referred to as a curing agent or a vulcanising agent. Generally, there exist two main types of silicone rubber compositions which are heat vulcanised or high temperature vulcanising (HTV) silicone rubber compositions, often also referred to as high consistency rubber (HCR); and room temperature vulcanising (RTV) silicone rubber compositions.

[0003] HTV silicone rubber compositions are typically prepared by mixing the substantially linear high molecular weight silicone polymer with the filler and other desired additives to form a base or raw stock. Prior to use, the base is compounded to incorporate the crosslinking agent, other fillers, and additives such as pigments, anti-adhesive agents, plasticizers, and adhesion promoters; and it can be vulcanised by press vulcanisation or continuously by extrusion, i.e., injection and transfer moulding, to form the final silicone rubber product. For example, cable insulation is extruded by special techniques in which the silicone rubber is applied to cable cores by means of angular extruder heads.

[0004] The substantially linear high molecular weight silicone polymer most widely employed is a polysiloxane gum having a viscosity of 1,000,000 centistoke ( $\text{mm}^2/\text{s}$ ) or more. These polysiloxane gums generally contain alkyl groups, and unsaturated groups such as alkenyl groups, particularly vinyl groups and/or combinations of vinyl groups and hydroxyl groups to assist in their crosslinking. Such polysiloxane gums typically have a degree of polymerisation (DP) of 500-10,000, which represents the number of repeating units in the polymer.

[0005] Two types of fillers are used, i.e., reinforcing fillers are generally used alone or together with extending or non-reinforcing fillers. Reinforcing fillers impart high strength to vulcanised rubber and may comprise finely divided amorphous silica such as fumed silica and precipitated silica. Extending or non-reinforcing fillers are generally used to reduce the cost of the silicone rubber composition, and generally comprise inexpensive filler materials such as ground quartz, calcium carbonate, and diatomaceous earth. The reinforcing fillers are usually treated with organosilanes, organosiloxanes, or organosilazanes, in order to improve the physical and/or mechanical properties of the silicone rubber composition, i.e., tensile strength and compression set.

[0006] The crosslinking agents most widely used are organic peroxides which are capable of generating free radicals when heated to form crosslinks by reacting with the methyl and vinyl groups on the linear high molecular weight silicone polymer. Some commonly used organic peroxides are the non-vinyl specific organic peroxides such as benzoyl peroxide, 1,4-dichlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, di-*t*-butyl peroxide, dicumyl peroxide, tertiary butyl-perbenzoate, and monochlorobenzoyl peroxide; and the vinyl specific organic peroxides such as ditertiary-butyl peroxide, 2,5-bis-(tertiarybutyl-peroxy)-2,5-dimethylhexane, tertiary-butyl-trimethyl peroxide, tertiary-butyl-tertiary-butyl-tertiary-triphenyl peroxide, and *t*-butyl perbenzoate.

[0007] Silicone rubber compositions including HTV silicone rubber compositions can be and often are evaluated using various parameters including tensile strength which is the amount of force needed to break a rubber sample, elongation which is the length a rubber sample can be stretched, and compression set which is the amount of force needed for the permanent deformation of a rubber sample.

[0008] US Patent 4,677,141 (June 30, 1987) entitled "Method of Improving Heat Stability of Pigmentable Silicone Elastomer", assigned to the same assignee as the present invention, and hereinafter referred to as the '141 patent, is most representative of the above state of the art, over which the present invention is intended an improvement. The '141 patent describes a means of improving the heat stability of a pigmentable silicone elastomer

comprising a vinyl terminated organopolysiloxane polymer, a silica based reinforcing filler and an organic peroxide curing agent with a white clay such as kaolin which has been pretreated with olefinic unsaturated siloxy groups. There is disclosure in '141 which remotely suggests the possibility of replacing the reinforcing filler with kaolin.

5

[0009] In accordance with the present invention there is provided a method of making a treated kaolin containing silicone rubber composition consisting essentially of the steps of (i) mixing an organopolysiloxane and treated kaolin under room temperature conditions, the mixture prepared in (i) being free of reinforcing fillers; (ii) adding a crosslinking agent to the mixture in (i); and curing the mixture in (ii) at a temperature above room temperature by the application of heat.

10

[0010] It is to be understood that room temperature conditions means atmospheric pressure and a room temperature at normal ambient temperature of 20-25 °C (68-77 °F). It is a major advantage in the case of the present invention that heat is not required to be added during step (i) as is required when undertaking the in-situ treatment of reinforcing fillers. As in all mixing processes the effect of mixing will generate heat but mixing in the case of the present invention will not require any additional heat input.

15

[0011] The organopolysiloxane polymer comprises one or more polymers which preferably have the formula  $R_2R^1SiO[(R_2SiO)_x(RViSiO)]_ySiR_2R^1$  wherein each R is the same or different and is an alkyl group containing 1-6 carbon atoms, a phenyl group or a 3,3,3-trifluoroalkyl group, preferably each R group is a methyl or ethyl group;  $R^1$  is a hydroxy group or an alkenyl group, preferably vinyl or hexenyl group; x is an integer and y is zero or an integer and  $x + y$  is between 700 and 10 000. In one embodiment the organopolysiloxane is a mixture of two polysiloxane gums having the formulas  $R_2ViSiO[(R_2SiO)_x(RViSiO)]_ySiR_2Vi$  and  $R_2ViSi(R_2SiO)_xSiR_2Vi$  wherein R is an alkyl group containing 1-6 carbon atoms, Vi is vinyl, and x and y are 500-1,000.

25

[0012] Any suitable kaolin may be utilized, calcined kaolin is particularly preferred. As noted, it is an essential feature of the present invention to use a treated kaolin filler, in particular kaolin treated with one or more of the group comprising silane, silazane or short

30

chain organopolysiloxane polymers. Silanes found to be most suitable for the treatment of kaolin are alkoxysilanes of the general formula  $R(4-n)Si(OR)_n$ , wherein  $n$  has a value of 1-3; and each  $R$  is the same or different and represents a monovalent organic radical such as an alkyl group, an aryl group, or a functional group such as an alkenyl group, e.g. vinyl or allyl, an amino group or an amido group. Some suitable silanes therefore include alkyltrialkoxysilanes such as methyltriethoxysilane, methyltrimethoxysilane, phenyltrialkoxysilanes such as phenyltrimethoxysilane, or alkenyltrialkoxysilanes such as vinyltriethoxysilane, and vinyltrimethoxysilane. If desired, silazanes can also be used as treating agents for the kaolin filler, such as hexamethyldisilazane; 1,1,3,3-tetramethyldisilazane; and 1,3-divinyldimethyldisilazane. Short chain organopolysiloxanes might for example include hydroxy terminated polydimethylsiloxanes having a degree of polymerisation of from 2 to 20, hydroxy terminated polydialkyl alkylalkenylsiloxanes having a degree of polymerisation of from 2 to 20 and organopolysiloxanes comprising at least one Si-H group, which may or may not be a terminal group.

**[0013]** A crosslinking agent, as noted above, is required and compounds which can be used herein include organic peroxides such as dialkyl peroxides, diphenyl peroxides, benzoyl peroxide, 1,4-dichlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, di-*t*-butyl peroxide, dicumyl peroxide, tertiary butyl-perbenzoate, monochlorobenzoyl peroxide, ditertiary-butyl peroxide, 2,5-bis-(tertiarybutyl-peroxy)-2,5-dimethylhexane, tertiary-butyl-trimethyl peroxide, tertiary-butyl-tertiary-butyl-tertiary-triphenyl peroxide, and *t*-butyl perbenzoate. The most suitable crosslinking agents are benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, di-*t*-butyl peroxide, and dicumyl peroxide.

**[0014]** The present compositions can also be cured and/or crosslinked by a platinum group metal catalysed hydrosilylation reaction using an organohydrogensiloxane as the crosslinking agent instead of the organic peroxide. To effect curing of the present composition, the organohydrogensiloxane must contain more than two silicon bonded hydrogen atoms per molecule. The organohydrogensiloxane can contain, for example, from about 4-20 silicon atoms per molecule, and have a viscosity of up to about 10 Pa.s at 25 °C. The silicon-bonded organic groups present in the organohydrogensiloxane can include

substituted and unsubstituted alkyl groups of 1-4 carbon atoms that are otherwise free of ethylenic or acetylenic unsaturation.

5 [0015] Platinum group metal containing catalysts useful to catalyse curing of the present compositions can be any of those known to catalyse reactions of silicon bonded hydrogen atoms with silicon bonded alkenyl groups. The preferred platinum group metal for use as a catalyst to effect cure of the present compositions by hydrosilation is platinum. Some preferred hydrosilation catalysts for curing the present composition are platinum metal, platinum compounds and platinum complexes. Representative platinum compounds include  
10 chloroplatinic acid, chloroplatinic acid hexahydrate, platinum dichloride, and complexes of such compounds containing low molecular weight vinyl containing organosiloxanes.

[0016] The platinum group metal containing catalyst may be added to the present composition in an amount equivalent to as little as 0.001 part by weight of elemental  
15 platinum group metal, per one million parts (ppm) of the composition. Preferably, the concentration of platinum group metal in the composition is that capable of providing the equivalent of at least 1 part per million of elemental platinum group metal. A catalyst concentration providing the equivalent of about 3-50 parts per million of elemental platinum group metal is generally the amount preferred.

20 [0017] This curing alternative is known in the art, and reference can be had to US Patent 5,863,968 (January 26, 1999), for example.

[0018] Preferably the mixture in (i) is free of silica and/or or other fillers. However  
25 the composition may comprise up to 5 parts per weight per 100 parts by weight of polymer + treated kaolin. Preferably when present the rheology modifier is present in an amount of from 1 to 3 parts by weight per 100 parts by weight of polymer + treated kaolin. The rheology modifier may comprise polytetrafluoroethylene (PTFE), boric acid, amorphous precipitated or fumed silica. It is to be understood that the amount of silica present within the  
30 ranges permitted are such that it is present in such low amounts so as to have a negligible effect on the physical properties of the resulting composition.



[0019] Other additives which where appropriate may be utilized include pigments and colouring agents, anti-adhesive agents, plasticizers, and adhesion promoters.

5 [0020] Silicone rubber compositions having equivalent mechanical properties to conventional silicone rubber compositions can be produced according to the present invention in a process which involves no heat, and which avoids the necessity to use expensive fumed silica as a reinforcing filler.

10 [0021] The conventional route of preparing highly filled silicone rubber compositions is to first make a silicone rubber base by heating a mixture of fumed silica, a treating agent for the silica, and an organopolysiloxane e.g. a polysiloxane gum in a mixer. The silicone rubber base is removed from the first mixer and transferred to a second mixer where generally about 150 parts by weight of a non-reinforcing or extending filler such as ground quartz is added per 100 parts by weight of the silicone rubber base. Other additives are  
15 typically fed to the second mixer such as crosslinking agents, pigments and colouring agents, heat stabilizers, anti-adhesive agents, plasticizers, and adhesion promoters.

[0022] The mechanical properties of these finished compositions are known to be generally much lower than the mechanical properties of the silicone rubber base. Thus,  
20 highly filled silicone rubber base compositions have relatively high mechanical properties generally represented by a tensile strength in excess of about 8 MPa, an elongation at break in excess of 300 percent, a tear strength greater than 20 kNm<sup>-1</sup>, a hardness (Shore A) of 40-80, and a density of 1.1-1.2 gcm<sup>-3</sup>. However, it is well known that upon compounding of the silicone rubber base into a finished composition, the resulting composition will exhibit  
25 mechanical properties which are less than those of the corresponding silicone rubber base, i.e., a tensile strength of 5-7 Mpa, an elongation at break of 180-300 percent, a tear strength of 10-20 kNm<sup>-1</sup>, a hardness (Shore A) of 60-90, and a density of 1.2-1.8 gcm<sup>-3</sup>.

[0023] Yet, according to this invention, it is still possible to obtain acceptable levels  
30 of mechanical, thermal, and electrical properties, generally represented by property profiles with values such as a tensile strength in excess of 6 Mpa; a hardness (Shore A) of 40-80; a density of 1.1-1.5 gcm<sup>-3</sup>; a dielectric strength greater than about 25 kv; an elongation greater

than 150 percent, and a compression set of less than 30 percent, after heat ageing for 240 hours in air at 200 °C.

[0024] In the process according to the invention, the necessity of making a silicone rubber base containing fumed silica, and then another composition containing a secondary non-reinforcing or semi-reinforcing filler is avoided. Rather, a treated semi-reinforcing kaolin filler is mixed directly with the organopolysiloxane, e.g. polysiloxane gum to produce a finished composition with mechanical properties equivalent to conventional silicone rubber compositions. In addition, the necessity of applying heat is avoided, and the entire process can be carried out quickly and efficiently in a single mixing device.

[0025] Because kaolin disperses much more easily than fumed silica in polysiloxane gums, the total mixing cycle is considerably reduced, giving much greater mixer utilization. In addition, since kaolin is a semi-reinforcing filler, it is capable of providing a finished composition having adequate mechanical properties. However, because kaolin is only semi-reinforcing, a higher loading level needs to be used than would be the case for fumed silica. On the other hand, because of the lower cost of kaolin compared to silica, it is not necessary to use a large amount of kaolin to obtain the right level of economic attractiveness for the finished composition. Preferably the ratio of treated kaolin to organopolysiloxane is from 1:2 to 2:1. Thus, one is enabled to use, for example, about 100 parts by weight of kaolin in 100 parts by weight of the organopolysiloxane e.g. polysiloxane gum, without using fumed silica.

[0026] The same level of mechanical properties can thereby be obtained as with finished compositions containing fumed silica. Furthermore, the elimination of fumed silica means that no heating is required, and the whole compounding process can be carried out in a single mixer. In addition, the incorporation time for kaolin is much higher than for fumed silica, with the result that mixer capacity is increased by utilizing the faster throughput. Finally kaolin has a much higher bulk density than fumed silica, which allows much improved ease of handling and storage.

[0027] These finished kaolin containing silicone rubber compositions are useful in applications such as silicone profile extrusions, wire and cable coatings, glazing, and for

construction gaskets. The only requirement relative to its use is that the finished composition have a property profile roughly equivalent to that acceptable for the particular application.

[0028] The features that distinguish the method of this invention from that described in the '141 patent are that the only filler present a silane treated kaolin, no heat is applied, the process is free reinforcing fillers such as silica and free of secondary fillers such as ground quartz.

[0029] Kaolin is well known in the art and is adequately described in the '141 patent incorporated by reference. Polysiloxane gums used for the preparation of silicone rubber are also well known in the art and are also adequately described in the '141 patent incorporated by reference.

[0030] Representative polysiloxane gums preferred according to the invention are high molecular weight gums with the formula  $\text{Me}_2\text{ViSiO}[(\text{Me}_2\text{SiO})_x(\text{MeViSiO})]_y\text{SiMe}_2\text{Vi}$  and high molecular weight gums of the formula  $\text{Me}_2\text{ViSi}(\text{Me}_2\text{SiO})_x\text{SiMe}_2\text{Vi}$  wherein Me represents the methyl group  $-\text{CH}_3$ , Vi represents the vinyl group  $\text{CH}_2=\text{CH}-$ , and the degree of polymerisation (DP) is approximately 1,000, i.e., DP corresponds to the value of x or the sum of x and y.

[0031] Three kaolin compositions were used in the accompanying examples to illustrate the method of the invention. The kaolins were products manufactured and distributed by Imerys Minerals Limited, Cornwall, United Kingdom. All of the kaolins were composed of calcined kaolin and differed only in the particulars of the process of calcination and the particle size.

[0032] All of the examples were carried out using silicone rubber compositions having the same formulation. The formulation consisted of 100 parts by weight of kaolin and 100 parts by weight of polysiloxane gum. The polysiloxane gum consisted of a mixture of equal parts by weight of one polysiloxane gum with the first formula shown above and equal parts by weight of another polysiloxane gum with the second formula shown above. The silicone rubber compositions were prepared by mixing the ingredients in a Braebender®

mixer for 30 minutes. No heat was applied or used during the process. It was all carried out at the existing room temperature.

[0033] As used herein, the term *room temperature* is intended to mean the normal ambient temperature of from 20-25 °C (68-77 °F). The mixed silicone rubber compositions were then press cured into sheets at 116 °C for five minutes using 0.6 parts by weight of 2,4-dichlorobenzoyl peroxide crosslinking agent. The sheets were post cured at 200 °C for four hours before being subjected to testing and evaluation.

10 [0034] The test results shown in the tables reflect the changes in properties of the test sheets on heat ageing of the sheets in air at 200 °C for periods of up to about 240 hours. The properties evaluated were hardness, tensile strength, and elongation to break. Hardness was determined according to the international standard for hardness measurements of rubber, plastic and other non-metallic materials, using a durometer described in the American Society  
15 for Testing and Material specification ASTM D2240, which is the recognized specification for the instrument and test procedure.

[0035] A typical property profile of silicone rubber compounds containing a silica based reinforcing filler and a non-reinforcing filler comprising e.g. quartz is shown in the  
20 following table as a guide:

Property Profile of Silicone Rubber Composition

Property	Value
Shore A Hardness	20-80
Density	1.1 to 1.5 gcm <sup>-3</sup>
Tensile Strength	> 6.0 MPa
Elongation at Break	> 150 Percent
Compression Set	< 30 Percent after 22 hours at 177 °C
Dielectric Strength	> 25 kV
Thermal Stability	6.0 MPa and 150 Percent Elongation at Break after 10 days at 200 °C

## EXAMPLES

[0036] The following examples are set forth in order to illustrate the invention in more detail. As used herein, ASTM means the American Society for Testing and Materials, and DIN means the German Institute for Standardization.

### Preparation of Treated Kaolin - Procedure A

10 [0037] Calcined kaolin manufactured by Imerys Minerals Limited was placed in the mixing bowl of an ordinary domestic food mixer where it was vigorously stirred and agitated. Treating agent was then introduced into the mixing bowl with the kaolin, in a sufficient quantity to obtain the desired level of treatment of the kaolin surface. The mixer was left to run for 10 minutes after addition of the treating agent. The contents of the mixing bowl were  
15 then transferred to a metal tray, and placed in an air circulating oven at 120 °C for a minimum period of 12 hours.

### Preparation of Treated Kaolin - Procedure B

20 [0038] Procedure A was repeated except that the treated kaolin was not heat treated.

### Compounding

[0039] Filler (typically treated kaolin) prepared as described above, was mixed with a  
25 polydimethylsiloxane polymer (PDMS) in a Brabender internal mixer. In every case, the mixing procedure used was the same. According to the procedure, the mixer blades were initiated so as to rotate at maximum speed, the required quantity of PDMS was placed in the mixer, the required quantity of treated kaolin was added to the mixer, and once the kaolin addition had been completed, the mixer was allowed to run for an additional 30 minutes. The  
30 fill level of the mixer was kept constant by calculating the amount of kaolin and PDMS in volumetric terms. This was done on the assumption that the density of PDMS was 1.0 gcm<sup>-3</sup>, and that the density of the treated kaolin was 2.2 gcm<sup>-3</sup>.

### Testing of The Compounds

5 [0040] The treated kaolin compounds prepared as described above, were mixed with the suitable heat activated crosslinking agent(s) on a two-roll mill. The compounds were then crosslinked, and/or cured, into test sheets by the application of heat and pressure in a suitable mould.

### Example 1 - Untreated kaolin Filler

10

[0041] (i) Comparative tests were initially undertaken utilizing the following 5 potential fillers. 100 parts by weight of 5 different untreated extending fillers:

- i. Talc.
- ii. Quartz.
- 15 iii. Diatomaceous Earth.
- iv. Montmorillonite
- v. Kaolin

20 In each sample prepared 100 parts of the respective filler were mixed, as described above, with

a) 50 parts by weight of a dimethylvinylsiloxo terminated dimethylsiloxane-methylvinylsiloxane co-polymer (in which the mole ratio of dimethylsiloxane units to methylvinylsiloxane units was = 99.82:0.18) having an average degree of polymerisation (dp) of 7,000; and

25

b) 50 parts by weight of a dimethylvinylsiloxo terminated polydimethylsiloxane with an average dp of 7,000.

30 The resulting silicone rubber composition was vulcanised with 1.5 parts per 100gm of a mixture of 2,4-dichlorobenzoyl peroxide (50 % by weight) and silicone fluid, press moulded for 5 minutes at 116 °C under a pressure of 2 MPa to form a silicone rubber sheet with a

thickness of 2 mm, which was then placed for 4 hours in a heat-circulation type oven at 200 °C. Specimens were cut from the resultant sheet and mechanical properties were measured. Tensile and Elongation were determined by DIN 53 504. Durometer (Shore A) was determined by ASTM D2240. The montmorillonite extending filler inhibited the cure of 2,4-dichlorobenzoyl peroxide and as such did not cure. The results are shown in table 1.

Table 1a. Physical properties from typical extending fillers

Property	Talc	Quartz	Diatomaceous Earth	Montmorillonite	Kaolin
Durometer (Shore A)	50	42	66	DNC	57
Elongation (%)	147	174	136	DNC	163
Tensile Strength (Mpa)	4.5	4.0	4.7	DNC	6.1

10 DNC =Did Not Cure

[0042] Table 1a shows a range of physical properties which were measured from a selection of commercially available mineral fillers it will be noted that of the fillers used only kaolin was able to provide a silicone rubber having the required physical properties. It is to be noted that in particular untreated kaolin filler silicone rubber gave significantly better tensile strength results.

[0043] In view of the latter the untreated kaolin samples were further analysed with respect to the effect of heat aging on the mechanical properties of the untreated kaolin filled silicone rubbers

[0044] Specimens were also subjected to heat treatment in a heat circulating oven at temperatures of 200 °C for 3 day, 7 day, and 10 day times of duration whereupon the mechanical properties were re-measured, and the percent difference was determined. The results are shown in Table 1 Example 1 was repeated except that 100 parts by weight of an

untreated kaolin filler was used. In addition, the specimens were subjected to heat treatment in a heat circulating oven at 200 °C for 3 day, 7 day, and 10 day times of duration.

Table 1b – Mechanical Properties of Untreated Kaolin - Initially and After Heat Aging for 3,7 and 10 days at 200 °C

Property	Initial	Three Day Percent Difference	Seven Day Percent Difference	Ten Day Percent Difference
Durometer (Shore A)	57	+44	+58	+39
Elongation (percent)	163	-56.0	-79.0	-78
Tensile (Mpa)	6.1	-16.4	-28.0	-38

[0045] It will be seen that whilst the initial mechanical properties fall with the required range of values when using untreated kaolin, heat aging results in the rubber becoming brittle and disintegrating as it is no longer elastomeric as seen by the fact that the hardness significantly increases and the elongation and tensile strength of the rubber containing untreated kaolin loses the majority of its elongation properties and a substantial proportion of its tensile strength. Hence, untreated kaolin may not be used for applications involving heat treatments.

#### Example 2

##### Effect of Treatment Level Using Phenyltrimethoxysilane

[0046] 100 parts by weight of treated kaolin filler with treatment levels of phenyltrimethoxysilane of 3.7 gram, 7.4 gram, and 9.3 gram per 100 grams of kaolin were prepared as described above in Procedure A, and mixed, as described above, with

- a) 50 parts by weight of a dimethylvinylsiloxy terminated dimethylsiloxane-methylvinylsiloxane copolymer, in which the mole ratio of dimethylsiloxane



units to methylvinylsiloxane units was 99.82:0.18, with an average dp of 7,000; and

- b) 50 parts by weight of a dimethylvinylsiloxyl terminated polydimethylsiloxane with an average dp of 7,000, having both of its terminal ends of the molecular chain endblocked by dimethylvinylsiloxyl groups.

[0047] The resulting silicone rubber composition was vulcanised with 1.5 parts per 100 grams of a mixture containing 50 percent by weight of 2,4-dichlorobenzoyl peroxide and 50 percent by weight of a silicone fluid. It was press moulded for 5 minutes at 116 °C under a pressure of 2 Mpa, and formed a silicone rubber sheet with a thickness of 2 mm. The sheet was then placed in a heat circulation oven for four hours at 200 °C. Specimens were cut from the resultant sheet, and its mechanical properties were measured. Tensile Strength and Elongation to Break were determined by DIN 53 504. Durometer (Shore A) Hardness was determined by ASTM D2240, and Tear Strength was determined by ASTM D624B. Specimens were also subjected to heat treatment in a heat circulating oven at temperatures of 200 °C for 10 days, whereupon the mechanical properties were re-measured, and the percent difference was determined. The results are shown in Table 2.

Table 2- Effect of Treatment Level of Phenyltrimethoxysilane on Mechanical Properties - Initially and After Heat Aging at 200 °C

Property	3.7 grams of Silane per 100 grams of kaolin	7.4 grams of Silane per 100 grams of kaolin	9.3 grams of Silane per 100 grams of kaolin
Durometer (Shore A)	54	52	58
Elongation (percent)	164	178	185
Tensile (Mpa)	6	6.1	5.3
Tear (kN/m)	13.4	12.18	12.79
Percent difference after aging @ 200°C for 10 days			
Durometer (Shore A)	+ 66.7	+ 11.53	0
Elongation (percent)	- 40.24	- 12.35	+ 11.32
Tensile (Mpa)	+ 6.6	+ 4.91	+ 5.0

**Example 3 - Effect of Treatment Level Using Methyltrimethoxysilane**

[0048] Example 2 with the exception that 100 parts by weight of treated kaolin filler with treatment levels of methyltrimethoxysilane of 3.8 gram, 5.1 gram, and 6.4 gram per 100 grams of kaolin, was used. The results are shown in Table 3.

**Table 3 – Effect of Treatment Level of Methyltrimethoxysilane on Mechanical Properties - Initially and After Heat Aging at 200 °C**

Property	3.8 grams of Silane per 100 grams of kaolin	5.1 grams of Silane per 100 grams of kaolin	6.4 grams of Silane per 100 grams of kaolin
Durometer (Shore A)	58	59	59
Elongation (percent)	161	153	152
Tensile (Mpa)	6.7	6.3	6.2
Tear (kN/m)	11.63	12.2	13.12
Percent difference after aging @ 200°C for 10 days			
Durometer (Shore A)	+ 15.5	+ 15.3	+ 11.86
Elongation (percent)	- 15.5	- 9.15	- 23.68
Tensile (Mpa)	- 3.0	0	- 12.90

**Example 4 - Effect of Treatment Level With Phenyltrimethoxysilane and Vinyltrimethoxysilane**

[0049] Example 2 was repeated with the exception that 100 parts by weight of treated kaolin filler with treatment levels of a mixture of phenyltrimethoxysilane and vinyltrimethoxysilane was used. The results are shown in Table 4. Treatment A is 2.77 grams of vinyltrimethoxysilane per 100 grams of kaolin; Treatment B is 2.77 grams of vinyltrimethoxysilane per 100 grams of kaolin and 0.92 grams of phenyltrimethoxysilane per 100 grams of kaolin; Treatment C is 2.77 grams of vinyltrimethoxysilane per 100 grams of

kaolin and 1.84 grams of phenyltrimethoxysilane per 100 grams of kaolin; and Treatment D is 2.77 grams of vinyltrimethoxysilane per 100 grams of kaolin and 3.73 grams of phenyltrimethoxysilane per 100 grams of kaolin.

5 Table 4 - Effect of Treatment ratio level on Mechanical Properties - Initially and After Heat Aging at 200 °C

Property	Treatment A	Treatment B	Treatment C	Treatment D
Durometer (Shore A)	59	59	59	57
Elongation (percent)	152	133	153	158
Tensile (Mpa)	6.3	5.9	6.5	6.4
Tear (kN/m)	16.5	13.8	13.6	13.0
Percent difference after aging @ 200°C for 10 days				
Durometer (Shore A)	+ 42.4	+ 37.2	+ 32.2	+ 31.6
Elongation (percent)	- 23.0	- 14.3	- 20.9	- 22.8
Tensile (Mpa)	- 7.9	- 6.8	- 12.2	- 20.6

Example 5 - Effect of Crosslinking Agents on the Cure Characteristics of

10 Phenyltrimethoxysilane Treated kaolin

[0050] Example 2 was repeated with the exception that 100 parts by weight of treated kaolin filler with a treatment level of phenyltrimethoxysilane of 3.7 grams per 100 grams of the kaolin was used. In addition, the resulting silicone rubber composition was vulcanised

15 and cured under different conditions using four different organic peroxide systems as follows:

(i) 1.5 parts per 100 grams of a mixture containing 50 percent by weight of 2,4-dichlorobenzoyl peroxide and 50 percent by weight of a silicone fluid, and cured for 5 minutes at 116 °C,

5 (ii) 1.5 parts per 100 grams of a mixture of containing 40 percent by weight of dicumyl peroxide and 60 percent by weight of a silicone fluid, and cured for 10 minutes at 150 °C,

10 (iii) 1.0 part per 100 grams of a mixture containing 50 percent by weight of dibenzoyl peroxide and 50 percent by weight of a silicone fluid, and cured for 5 minutes at 127 °C, and

15 (iv) 1.0 part per 100 grams of a mixture containing 45 percent by weight of 2,5-bis (t-butyl peroxy)-2,5-dimethyl hexane and 55 percent by weight of a silicone fluid, and cured for 10 minutes at 171 °C.

[0051] A moving die rheometer, Model MDR 2000E manufactured by Alfa Technologies Inc. was used to achieve a maximum torque value which is indicative of the final state of vulcanisation. The torque/time values were measured at 0 percent, 10 percent, and 90 percent, of the final torque value and are an indicator of the rate of cure. The results are shown in Table 5. In Table 5, DCBP is 2,4-dichlorobenzoyl peroxide, DCP is dicumyl peroxide, DBP is dibenzoyl peroxide, and BTBP is 2,5-bis-(t-butyl peroxy)-2,5-dimethylhexane.

**Table 5 - Effect of Crosslinking Agents on the Cure Characteristics of Treated kaolin**

Measurement	DCBP	DCP	DBP	BTBP
Time to reach indicated extent of cure* (metric minutes)				
10 percent	0.33	9.51	0.34	0.57
90 percent	0.86	9.50	1.12	5.58
100 percent	5	10	5	10
MDR Torque values at different extents of cure				
0 percent	1.27	0.95	1.15	0.65
10 percent	2.46	0.19	0.81	0.37
90 percent	16.97	0.20	15.08	5.11
100 percent	18.76	0.19	16.69	5.63
* Indicates that 100 percent cure is considered the torque value at the end point of the test				

**5 Example 6 - Effect of Treated Kaolin Filler in a Low Viscosity Silicone Polymer**

[0052] 200 parts by weight of a treated kaolin filler with a treatment level of 3.7 grams of phenyltrimethoxysilane per 100 grams of the kaolin, was prepared as described above in Procedure A. The treated kaolin was mixed with 100 parts by weight of a dimethylvinylsiloxyl terminated polydimethylsiloxane with an average dp of about 850, using a Brabender mixer operated at a mixing speed of 120 revolutions per minute/12.6 radian per second. After a mixing time of 70 minutes, an additional 100 parts by weight of a dimethylvinylsiloxyl terminated dimethylsiloxane-methylvinylsiloxane co-polymer in which the mole ratio of dimethylsiloxane units to methylvinylsiloxane units was 99.82:0.18, having an average dp of 7,000, was put into the mixer.

[0053] The resulting silicone rubber composition was vulcanised with 1.5 parts per 100 grams of a mixture of 50 percent by weight of 2,4-dichlorobenzoyl peroxide and 50 percent by weight of a silicone fluid. It was press moulded for 5 minutes at 116 °C under a pressure of 2 MPa and formed a silicone rubber sheet with a thickness of 2 mm. The sheet was then placed in a heat circulation oven for 4 hours at 200 °C. Specimens were cut from the

sheet and mechanical properties were measured. Tensile Strength and Elongation to Break where determined by DIN 53 504. Durometer (Shore A) Hardness was determined by ASTM D2240. The results are shown in Table 6.

5 Table 6 - Effect of Treated Kaolin Filler in the Low Viscosity Silicone Polymer of Example 6

Property	Elastomer Containing a Treated Kaolin Filler
Durometer (Shore A)	59
Elongation (percent)	177
Tensile (Mpa)	7.0
Tear (kN/m)	13.6

10 [0054] The results shown above in these Examples indicate that the silicone rubber compositions according to the invention have equivalent mechanical properties to conventional silicone rubber compositions, but can be produced in a process which avoids the need for heating and the necessity to use expensive fumed silica as a filler.

15 [0055] Other variations may be made in compounds, compositions, and methods described herein without departing from the essential features of the invention. The embodiments of the invention specifically illustrated herein are exemplary only and not intended as limitations on their scope except as defined in the appended claims.

# CLAIMS

1. A method of making a treated kaolin containing silicone rubber composition consisting essentially of the steps of (i) mixing an organopolysiloxane and treated kaolin under room temperature conditions, the mixture prepared in (i) being free of reinforcing fillers; (ii) adding a crosslinking agent to the mixture in (i); and curing the mixture in (ii) at a temperature above room temperature by the application of heat.
2. A method according to Claim 1 in which room temperature is normal ambient temperature of 20-25 °C (68-77 °F).
3. A method according to Claim 1 in which the polysiloxane gum comprises a mixture of two polysiloxane gums having the formula  $R_2ViSiO[(R_2SiO)_x(RViSiO)]_ySiR_2Vi$  and the formula  $R_2ViSi(R_2SiO)_xSiR_2Vi$  wherein in each formula, R represents an alkyl group containing 1-6 carbon atoms; Vi represents the vinyl group; and x and y each have values of 500-1,000.
4. A method according to Claim 1 in which the crosslinking agent is a peroxide selected from the group consisting of benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, di-*t*-butyl peroxide, and dicumyl peroxide.
5. A method according to Claim 1 in which the kaolin comprises a kaolin treated with an alkoxysilane of the formula  $R(4-n)Si(OR)_n$  wherein n has a value of 1-3; and R is an alkyl group, an aryl group, or an alkenyl group.
6. A method according to Claim 5 in which the alkoxysilane is a compound selected from the group consisting of methyltriethoxysilane, methyltrimethoxysilane, phenyltrimethoxysilane, vinyltriethoxysilane, and vinyltrimethoxysilane.

7. A method according to Claim 1 wherein the mixture in (i) comprises about equal amounts of polysiloxane gum and kaolin.
8. A method according to Claim 1 in which the crosslinking agent is an organohydrogensiloxane crosslinking agent, and a platinum group metal hydrosilylation catalyst is added in an amount sufficient to cure the composition.
9. A method as hereinbefore described with reference to examples 2 to 6.



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